Ph.D. Synopsis

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1.0. Title of the thesis

"Analytical Studies on Some Ionic Species Employing Attenuated Total Reflectance (ATR)-Fourier Transform Infrared (FTIR) Technique"

2.0. Introduction

There are many types of ionic species (non metallic inorganic oxides) such as nitrate (NO_3^-), sulphate (SO_4^{2-}), borate (BO_3^{3-}) and phosphate (PO_4^{3-}) etc., in the environment, which are considered to be environmental pollutants (De, 2003). Many ionic species such as SO_4^{2-}, used in agriculture as fungicide, algaecide and nutrition supplement in fertilizers, are toxic (Lodhi *et al.*, 2006). NO_3^- is one of the most frequent groundwater pollutants in rural areas (Borenstein *et al.*, 2006). It needs to be regulated in drinking water basically because excess levels can cause methaemoglobinaemia or "blue baby" disease (Linker *et al.*, 2006). BO_3^{3-} is not only acutely toxic; a significant dose of the chemical causes severe symptoms of ailments or eventual death (Klotz *et al.*, 2000). In environment phosphates have various types of direct and indirect effects on human and plants (Nyholm, 1991).

Thus, the need for new procedures on determination of ionic species such as NO_3^-, SO_4^{2-}, $BO_3^{3-}$and PO_4^{3-} etc. with low detection limit, high sample throughput, applicability to low sample size etc. in real samples is always a challenge to the analytical chemists.

Many techniques have been reported for the determination of a large number of ionic species in wide variety of samples such as flow injection analysis (Haghighi and Tavassoli , 2001), capillary electrophoresis (Nakashima *et al.*, 2001), ion chromatography (Jackson, 2000; Neal *et al.*, 2007), gas chromatography (Chakraborti *et al.*, 1984), mass spectroscopy (Smith *et al.*, 1990) and turbidimetry method (Morais *et al.*, 2001), various spectrophotometric techniques viz. catalytic, fluoresnce, kinetic and uv-vis spectrophotometry (Ensafi *et al.*, 2004, Nakaya *et al.*, 2011, Goncharuk *et al.*, 2009, Manual, UK Env Agency 2011, Afkhami *et al.*, 2007). However, these techniques contain inherent drawbacks such as high detection limit, requirement large sample size, low sensitivity and interferences of other ions etc.

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. FTIR is very reliable for the characterization, identification and also quantification of the acquired data (Shai, 2012). FTIR is an analytical technique used to identify mainly organic and inorganic materials, which provides information about the chemical bonds and molecular structure of a material (Duarte *et al.*, 2002). The FTIR spectrum is equivalent to the "fingerprint" of the material and can be compared with cataloged FTIR spectra to identify the material. An

FTIR Spectrometer is an instrument which acquires broadband NIR to FIR spectra (Kouyomdjian and Saliba, 2005).

The recent advent of a special reflection technique, namely Attenuated Total Reflectance (ATR), has greatly facilitated the application of infrared spectroscopy to many organic and inorganic species (Puttnam *et al.*, 1965, Brancaleon *et al.*, 2001). With Attenuated Total Reflection Fourier Transform Infrared spectroscopy (ATR-FTIR), species adsorbed on the surface of an ATR crystal are detected by an evanescent wave with a typical penetration depth of ~ 0.5 mm. This standing wave is a result of internal reflection of the infrared light in the crystal. Due to multiple reflections, the sensitivity of the technique is enhanced. Figure 1 shows the internal beam path of infrared and the transitory wave of an ATR crystal. The ATR mode is one of the sampling approaches in FTIR imaging (Feng *et al.*, 2009, Iizasa *et al.*, 2010, Johnston *et al.*, 2001, Zhao *et al.*, 2012). Amazingly, recent studies revealed important applications of FTIR in the analysis of inorganic chemical species such as NO_3^-, SO_4^{2-}, $BO_3^{3-}$and PO_4^{3-} etc. in airborne solid (Kouyomdjian and Saliba, 2005). Table 1 shows the comparative features on the determination of some of the ionic species by different techniques.

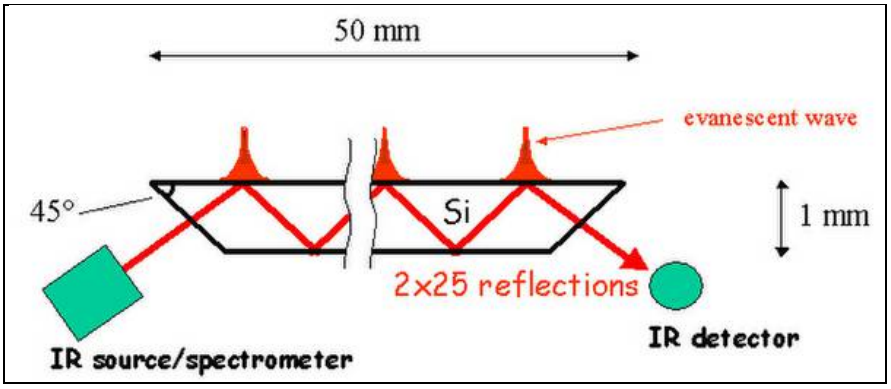

Figure1. An ATR crystal showing the infrared beam path and the evanescent wave.

All multi atomic ions are infrared active, which have a unique property of changing dipole moment directions as a result of molecular vibration in specific region between 4500-400 cm^{-1} (Huth *et al.*, 2012). Thus, this unique characteristic behavior of these ions will be explored during the proposed investigation, for their qualitative and quantitative analysis, by the Attenuated Total Reflectance (ATR)-Fourier Transforms Infrared (FTIR) technique.

Table 1. Comparison of analytical features of ionic species using different techniques.

S. No.	Species Determined	Techniques Employed	Reagents Used	Limit of Detection (LOD)/ Linear Dynamic Range (LDR)	Applications	References
1.	NO_3^-	Flow-injection gas-phase molecular absorption spectrometry	On-line copperized cadmium (Cd-Cu) reduction column	LOD: 2.97 µg ml^{-1}	waters	Haghighi and Tavassoli , 2001
2.	NO_3^-, NO_2^-	Catalytic spectrophotometry	Redox reaction between pyrogallol-sulfonephthalein and potassium bromate in acidic media; 465 nm	LDR: 2.4 to 160 ng ml^{-1} of nitrite and 4.0 to 100 ng ml^{-1} of nitrate	food and water samples	Ensafi *et al.*, 2004
3.	NO_3^-	Diffuse reflectance fourier transform infrared spect (DRS-FTIR)	KBr substrate	LOD: 0.07 μg g^{-1}	soil, dry deposits and aerosol samples	Verma and Deb, 2007
4.	SO_4^{2-}	Turbidimetric-Nephelometric flow injection analysis	Precipitating agent-barium chloride in polyvinyl alcohol	-	natural and residual water	Morais *et al.*, 2001
5.	SO_4^{2-}	Diffuse reflectance fourier transform infrared spec (DRS-FTIR)	KBr substrate	LOD: 0.20 μg g−1	environmen-tal samples	Verma and Deb, 2007
6.	SO_3^{2-}	Diffuse reflectance fourier transform infrared spec (DRS-FTIR)	KBr substrate	LDR: 50–5000 ng/10 μL	alcoholic beverages	Verma and Deb, 2009
7.	Br^-, Cl^-, F^-, NO_3^-, SO_4^{2-}	Ion Chromatograph	IC column	LOD: Cl^- (0.2), NO_3^- (0.1), SO_4^{2-} (0.2), F^- (0.01), Br^-(0.01 mg l^{-1})	rain, cloud, river waters	Neal *et al.*, 2007
8.	F^-	Fluorescence spectrophotometer λ(ex) 503 nm and λ(em) 527 nm	2',7'-Dichloro-fluorescein di-tert-butyldimethylsilyl ether	LOD: 1.0×10^{-6} M	river and tap water samples	Nakaya *et al.*, 2011
9.	PO_4^{3-}	Capillary electrophoretic UV detection at 220nm	Formation of a Keggin-type $[PMo_{12}O_{40}]^{3-}$ complex	LOD: 1 x 10^{-7} M	river water	Nakashima *et al.*, 2001
10.	ClO_4^-	Vis-Spectrophotometry	Ion associate with crystal violate in dichlorobenzene 595 nm	LOD: 10-100 µg dm^{-3}	river water and soil	Goncharuk *et al.*, 2009
11.	CN^-	Vis-Spectrophotometry	Chloramines-T, Barbituric acid, 575 - 600 nm	LOD: 0.5 mg kg^{-1}	soil	Manual, UK Env Agency 2011
12.	CN^-, SCN^-	Kinetic spectrophotometry	PLS Model Chloramines-T, Barbituric acid 578 nm	LDR: 10.0–900.0 and 50.0-200.0 ng ml^{-1} for CN^- and SCN^- ions, respectively	water samples	Afkhami *et al.*, 2007

In the present work, some of the ionic species (e.g. NO_3^-, SO_4^{2-}, PO_4^{3-}, BO_3^{3-}, ClO_4^- etc.) will be tested for their qualitative identification and quantitative determination employing newly developed Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) technique. The methods will also be tested towards some real samples e.g. waters, sediments, soil, food and food product etc.

3.0. Objectives

The main objectives of the proposed work may be summarized as follows:

1. Detection of important IR active peaks of chemical species at very low level; proper selection of qualitative analytical peaks in infrared region (7000-400 cm^{-1}).
2. Determination of the non metallic ionic species (e.g. NO_3^-, SO_4^{2-}, BO_3^{3-} and PO_4^{3-} etc.) at trace level employing ATR-FTIR technique on KBr or zinc selenide substrates.
3. Calibration curves for analysis using Kubelka-munk spectrum, studies on interionic effects, etc.
4. Test of analytical quality assurance (AQA) and statistical analysis for simultaneous analysis in real samples.
5. Application of the newly developed method to some real samples e.g. waters, sediments, soil, food and food product etc.

4.0. A brief review of the work already done in the field

4.1. International Status: Many international researchers have reported novel methods for analysis of many environmental species. Attenuated Total Reflection–Fourier Transform Infrared Spectroscopy as a possible method to investigate biophysical parameters of *stratum corneum* in vivo was reported by Brancaleon *et al.* (2001). Application of FTIR spectroscopy in environmental studies supported by two dimensional correlation analyses has done by Mecozzi *et al.* (2009). FTIR spectroscopy allow the analysis of a relevant amount of compositional and structural information concerning environmental samples (Koger-Kanaber, 2000) and joint use with 2DCORR has improved the performance of this technique in the studies of complex environmental systems (Noda and Ozaki, 2005). FTIR spectroscopy is recently uses in different analytical methods such as study of petroleum Heat-exchanger deposit (Tay and Kazarian, 2009),

diuron determination in commercial pesticide formulations (Armenta *et al.* 2005), investigation of coal component of Late Permian coals from Southern China (wang *et al.* 2001), for quantification of sugars in mango juice (Duarte *et al.* 2002). FTIR spectroscopy is also used for the comparative analysis of smokeless gunpowdwers (Lopez-Lopez *et al.* 2012). Chou *et al.* 2005, have shown the application of FTIR for size-segregated characterization of atmospheric aerosol. Maria *et al.* have done FTIR measurement of functional group and organic mass in aerosol samples over the Caribbean (Maria *et al.* 2002). McClenny has used FTIR for the detection of ammonium and sulphate in ambient aerosol collected on Teflon filters (McClenny, 1998). Polarized ATR-FTIR study of smectite in aqueous suspension was done by Cliff *et al.* 2001. Tasi and Kuo have developed the diffuse reflectance infrared Fourier transform spectroscopic method for rapid characterization of aerosols (Tasi and Kuo, 2006).

4.2. National Status: In Indian context, the application of FTIR has been made mainly as only a supporting tool for different analysis by several workers in diversified fields such as compound identification and structural elucidation (Thenmozhi et al., 2011, Arjunan *et al*., 2004), polymer studies (Charles *et al*. 2009, Patra et al. 2010), bioremedial processes and applications (Sultana *et al.*, 2011), geological studies (Saikia *et al.,* 2008, Palanivel and Velraj, 2007), biomedical applications, etc.

Some review articles on principle, technique, mathematics and application of FTIR spectroscopy is recently available (Sawant, 2011, Dole *et al.* 2011).

5.0. Noteworthy contributions in the field of proposed work

In our laboratory, many works have done in this field. Verma and Deb (2007) have determined nitrate in soil, dry deposits and aerosol samples using KBr matrix with diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS), which is rapid and precise analytical method for submicrogram level. Direct and rapid determination of sulphate in environmental samples with diffuse reflectance Fourier transform infrared spectroscopy using KBr substrate has been done by Verma and Deb (2007). Vanadium(V) and chromium(VI) have been successfully determined employing new combined single-drop micro-extraction and diffuse reflectance FTIR technique (Verma and Deb 2009; Verma *et al.* 2009).

Verma *et al.* (2008) have determined nitrogen dioxide in ambient air employing diffuse reflectance Fourier transform infrared spectroscopy. Single-drop and nanogram level determination of sulfite (SO_3^{2-}) in alcoholic and nonalcoholic beverage samples based on diffuse reflectance Fourier transform infrared spectroscopy (DRS-FTIR) analysis on KBr Matrix was established by Verma and Deb (2007). This method is absolutely free of uses of harmful and massive amounts of reagents and thus strongly supports the present day need of green chemistry. The exclusion of nitrogen from sample matrix by zirovalent iron nanoparticles and determination of ammonium has been effectively done by FTIR (Deb and Verma 2009).

6.0. Proposed methodology

In this proposed method there are no specific sample preparations required, sample can be directly put in ATR-FTIR and spectra may be obtained.

ATR-FTIR Determination of ionic species

The spectral studies of ionic species (such as NO_3^-, SO_4^{2-}, BO_3^{3-}, PO_4^{3-} ClO_4^-, etc.) into suitable solvent will be done using ATR-FTIR on KBr matrix or in a zinc selenide substrate. The ATR will be employed separately to check the differences in sensitivity of the methods. Table 2 shows the characteristic frequencies of some selected inorganic ions.

Analysis in KBr / Zinc selenide substrate

In our preliminary investigation, we used infrared spectrometric grade KBr as a matrix for the analysis, wherein all standards were poured into the finely ground and pre-weighed KBr for the matrix formation. This matrix was applied to the ATR directly for the spectral scanning. It was observed, interestingly, that there were no changes in the spectral position of the respective vibrational mode of chemical species when used as standard solution directly or after extraction with hydroxyamidine like complexing or chelating agents. This has shown the retention of the structural identity of such species even after complexation. The above scheme will be used also in the current research work for different chemical species. Comparative studies with different substrates like KBr and zinc selenide will be done to check sensitivity differences. Table 2 shows the characteristic peak of some ionic species.

Table 2. Infrared peaks (strong, sharp and weak) of some ionic species reported earlier[#]

S.No.	Ionic species	IR absorption peaks (cm^{-1})
1.	Nitrate	1730-1810 wk sp (SM), 1280-1520 stg (OD or M), 1020-1060 (owk) sp, 800-850 (W-M) sp, 715-770 wk-m* (OD)
2.	Sulphate	1040-1210 stg (OM or SMAX), (960-1030, often 1 or 2 wk sp bands), 570-680 m (OD or M)
3.	*o*-Phosphate	940-1120 stg (OM), 540-650 m (OD)
4.	Perchlorate	1050-1150 stg (O SMAX), 600-660 wk-m (OD)
5.	*tetra*-Borate	1340-1480 stg (SMAX), 1100-1150 wk-bd (OD), 1000-1050 wk-bd (OD), 900-950 w, ~825 wk, 520-545 wk, 500-505 wk, 450-470 wk

O = often, wk = weak, m = medium, stg = strong, bd = broad, sp = sharp, (OD) = often doublet, (M) = multiple, (SM) = sometimes multiple, (SMAX) = with submaxima.

(# Gadsden, 1975; Nakamoto, 1963; Nyquist and Kagel, 1971)

- ***Baseline correction for qualitative and quantitative analytical peaks***

On eyeballing to the spectral peaks to be obtained, qualitative as well as quantitative analytical peaks will be selected on the basis of simple reasons of sharp and intense spectral peaks in the observed regions of the IR scan. Further, for qualitative or quantitative analysis a two-point or multiple-point baseline corrections will be done in the selected region of IR scan.

7.0. Expected outcome of the proposed work

The following outcome of the proposed work may be summarized

- The proposed work will be cost effective because fewer amounts of chemicals and reagents will be used. The proposed work will also meet to the present day challenge of 'green-chemistry' which demands for creation of no or little pollution.
- This technique will enhance spatial resolution of the micro-ATR approach.
- The magnificence of the present work will remain with the need of very low volume and size of samples, i.e. 10 µg or 10 µl will be required for the analysis of the selected environmental pollutants.
- This technique will be very helpful in the term of speed, precision and accuracy.

8.0. References

Abbas A., Nahid S. and Reza Z.A.*; Talanta*, 71(2007), pp. 893.

Armenta S., Guillermo Q., Morales A., Garrigues S. and Guardia M.; *J. Agric. Food Chem.* 53(2005), pp. 5842.

Arjunan V., Subramanian S., Mohan S., *Spectrochim. Acta A: Mol. Biomol. Spectros.* **60** (2004) 995.

Borenstein A., Linker R., Shmulevich I. and Shaviv A.; *Appl. Specsc*., 60(2006), pp. 1267.

Brancaleon L., Bamberg M.P., Sakamaki T. and Kollias N.; *J. Invest. Dermatol*. 116(2001), pp. 380.

Chankraborti D., Jongle D., Vanmol W.E., Cleuvanbergen and Adams F.C.; *Anal. Chem.,* 56(1984), pp. 2692-2697.

Charles Julie, Ramkumaar G.R., Azhagiri S., Gunasekaran S., *E-Journal Chem.* **6**(1) (2009) 23.

De A.K.; *Environmental Chemistry,* 5th Ed., New Age International (P) Ltd., New Delhi, India,2003.

Deb M.K. and Verma D.; *Microchim. Acta,* 169(2010), pp. 23.

Dole Manjusha N., Patel Priyanka A., Sawant Sanjay D., Shedpure Priyanka S., *Adv. Appl. Fourier Transform Infrared Spectros.* **7** (2011) 159.

Duarte I.F., Borros A., Delgadillo I., Almeida C. and Gil A.M.; *J. Agric. Food Chem.*, 50(2002), pp. 3104.

Ensafi A.A., Rezaei B. and Nouroozi S. *Anal. Sci.,* 20(2004), pp. 1749.

Feng H., Tay and Kazarian S.G.; *Energy and Fuels*, 23(2009), pp. 4059.

Gadsden J.A., *Inorganic Spectra of Minerals and Related Inorganic Compounds*, printed and bound by R.J. Acford Ltd., Industrial Estate, Chichester, Sussex, 1975.

Goncharuk V.V., Zui O.V. and Kushchesvkaya N.F.; *J. Water Chem. Tech*., 31(2009), pp.184.

Haghighi B. and Fresenius T.A.; *J Anal Chem*., 371(2001), pp.1113.

Huth F., Govyadinov A., Amarie S. Nuansing W., Keilmann F., and Hillenbrand R.; *Nano Lett.*, 12(2012), pp. 3973.

Jackson P.E.; John Wiley and Sons Ltd., 2000, pp. 2779.

Jain A., Verma K.K.; *Anal. Chim. Acta,* 706(2011), pp. 37.

Johnston C.T. and Premachandra, *Soil Environ. Sci*., 17(2001), pp. 3712.

Klotz J.H., Greenberg L., Amrhein C. and Rust M.K.; *J. Econ. Entolmol*., 93(2000), pp. 1256.

Kogel-Knaber I.; *Org. Geochem*. 31(2000), pp. 609.

Kouyomdjian H. and Saliba N.A.; *Atmos. Chem. Phy. Discuss.* 5(2005), pp. 13053.

Lodhi H.S., Khan M.A., Verma R.S. and Sharma U.D.; *J. Environ. Biol.,* 27(2006), pp. 585.

Manual on 'The determination of cyanide and thiocyanate in soils and similar matrices' Methods for the Examination of Waters and Associated Materials, UK Environmental Agency 2011.

Mecozzi M., Moscato F., Pietroletti M., Quarto F., Oteri F. and Cicero A.M.; *Global Nest Journal* 11(2009), pp.593.

Morais, Ines P.A., Rangel, Antonio O.S.S., Souto and Renta M.S.*; J. AOAC Inter*., 84(2001), pp. 59.

Nakamoto K.; *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed., Wiley: New York , 1963.

Nakashima Y., Goto T., Kitazumi I. and Himeno S.; *Electrophoresis*, 22(2001), pp. 3377.

Nakaya M., Oshima M., Takayanagi T., Motomizu S. and Yamashita H.; *Talanta*., 84(2011), pp.1361.

Neal M., Neal C., Wickham H. and Harman S.; *Hydrol. Earth System Sci*., 11(2007), pp. 294.

Noda I, Ozaki I; *John Wiley & Sons*, UK (2005).

Nyholm N.; *Environ. Toxicol. Chem*., 10(1991), pp.581.

Nyquist R.A., Kagel R.O., *Infrared Spectra of Inorganic Compounds*, Academic Press, New York, 1971

Ottaway J.M. and Fell G.S.; *J. Pure Appl. Chem.* 58(1986), pp. 1707.

Palanivel R., Velraj G., *Indian J. Pure and Applied Phy.* **45** (2007) 501.

Patra K.C., Kumar K.J., Sahoo S.K., Suresh P., *Eurasian J. Anal. Chem.* 5(1) (2010) 73.

Puttnam N.A., Lee S. and Baxter B.H.; *J. Sol. Cosmatic Chemists*, 16(1965), pp. 607.

Saikia B.J., Parthasarathy G., Sarmah N.C., *Bull. Mater. Sci. © Indian Academy of Sciences* **31**(5) (2008) 775.

Sawant S.D., *Intern. J. Pharma. Biosci.* **2** (2011) 513.

Smith Richard D., Loo J.A., Edmonds C.G., Barinaga C.J., and Udseth H.R.; *Anal. Chem.,* 62(1990), pp. 882.

Sultana R. Raziya, Zafarullah S.N., Kirubamani N. Hephzibah, *Indian J. Sci. Technol.* **4**(8) (2011)967.

Tay F.H.and Kazarian S.G.; *Energy & Fuels,* 23(2009), pp. 4059.

Thenmozhi M., Bhavya P.K., Sivaraj Rajeshwari, *Intern. J. Engg. Sci. Technol.*, **3** (2011) 292.

Verma S.K. and Deb M.K.; *Anal. Chim. Acta,* 582(2007), pp. 382.

Verma S.K. and Deb M.K.; *Talanta* 71(2007), pp. 1546.

Zhao Y., Yuan J., Ji Z., Wang J., and Rohani S.; *Ind. Engg. Chem. Res*., 51(2012), pp. 12530.

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